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(54) Quaternary ammonium graft
polymers

(57) Water-soluble cationic
polyquaternary ammonium graft
copolymers are prepared by graft
polymerizing (a) one or more
water-soluble vinyl monomers onto (b)
a water-soluble cationic polyquaternary
ammonium polymer which contains
hydroxyalkylene groups.

(a) is typically acrylamide, optionally
mixed with acrylic acid, dimethyl diallyl
ammonium chloride and/or dimethyl
aminoethyl methacrylate
methosulphate.

(b) contains units of - A - CH₂ -
CH(OH).CH₂ - A - where A is tertiary or
quaternary nitrogen, and is typically the
quaternized reaction product of
epichlorhydrin with N,N,N',N' -
tetramethylene diamine and
optionally methylamine.

The polymers are useful as floccu-
lants, dry strength additives for paper,
and retention agents.

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SPECIFICATION

Quaternary ammonium graft polymers

5 The present invention relates to novel cationic graft copolymers and their uses for example as flocculants, dry strength additives for paper, and dye retention agents. More particularly, the present invention relates to quaternary ammonium graft 10 copolymers prepared by graft polymerizing water-soluble vinyl monomers to quaternary ammonium ionene type polymers. This invention is related to the flocculation of suspended matter by the aforesaid polymers, and to paper of improved 15 strength and dye retention prepared by use of the aforesaid polymers.

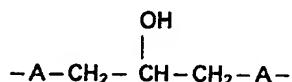
A number of methods are known in the art for the preparation of graft copolymers. These include 20 radiation methods, both high energy radiation from gamma rays or electron accelerators and actinic, i.e. photochemical radiation. Chemical catalysts which are also used include free radical initiator systems such as the ferrous ion-hydrogen peroxide reaction which is very effective in promoting graft 25 polymerization.

The present invention is not limited to any single method for initiation of the polymerization. However, the ceric ion initiation system taught by Mino, et al. (U.S. Patent No. 2,923,768) is particularly attractive. In this method it is believed that ceric ions react 30 directly with a pendant reactive group such as hydroxyl group on the polymeric substrate. The radical which results from this initial reaction then may react with vinyl monomers present in solution 35 yielding a graft copolymer. Relatively little homopolymer is produced by this technique unless large amounts of chain transfer agents are added.

It has now been discovered that certain polyquaternary ammonium polymers of the ionene type are 40 active substrates for graft polymerizations. Graft polymers produced by ceric ion-catalyzed graft polymerizations onto the aforesaid polyquaternary ammonium polymers are unusually effective as flocculants, dry strength agents for paper, and dye 45 retention agents.

Water-soluble cationic polymers have been used in a number of applications including the pulp and paper industry to increase strength and dye retention, in water treatment to flocculate suspended 50 solids, and in waste treatment to help dewater sludge. New materials which are effective in these applications are constantly being synthesized and evaluated, and materials with improved properties would be accepted readily.

55 The present invention provides water-soluble high-molecular-weight quaternary ammonium graft copolymers comprising a substrate portion and a graft portion. The substrate portion is derived from a water-soluble polymeric quaternary ammonium 60 composition having a plurality of hydroxypropylene groups having the structure



wherein A is a tertiary or quaternary nitrogen, and in which the number of quaternary nitrogen atoms exceeds the number of tertiary nitrogen atoms. The 65 graft portion is derived from a polymeric composition comprising polymerized water-soluble nonionic, anionic and/or cationic vinyl addition monomers. The amount of grafted vinyl addition polymer can vary between one-tenth and one hundred 70 times the amount of substrate polyquaternary ammonium polymer.

The above-described graft copolymers may be used to flocculate suspended inorganic and organic matter in aqueous solutions and may thus be useful 75 for flocculating impurities in water and in processing wastes. They can also be used for dewatering sewage sludge.

Furthermore, the copolymers of the invention may be useful in improving drainage and retention, e.g. 80 of fines, dyes, pigments, fillers and starch in the manufacture of paper and may thus be used to increase strength, improve sizing and increase the electroconductivity of paper and paperboard.

The present invention further provides a process 85 for the preparation of a graft copolymer as defined above which comprises reacting a water-soluble polymeric quaternary ammonium composition as defined in claim 1 with one or more water-soluble nonionic, anionic or cationic vinyl addition monomers, in the presence of a polymerisation catalyst.

The graft copolymers of the present invention 90 comprise a substrate portion, i.e., a previously made polymer, and a grafted portion. The substrate polymer is a cationic polyquaternary ammonium polymer of the ionen type. In general, these substrate polymers are made by the reaction of a ditertiary amine with epichlorohydrin. A convenient method to produce cationic polyquaternary ammonium polymers suitable for use in this invention is that described 95 by Buckman, et al. in U.S. Patent 4,054,542. Complete descriptions concerning the details of the reactant species as well as the methods of preparation are contained therein. These polymers have a molecular weight of approximately 40,000.

100 In addition to the polymers described above, other polymers described by Buckman, et al. in U.S. Patent 4,018,592 can be utilized. These polymer molecules have molecular weights in the range of 5,000.

A polyquaternary ammonium polymer may be 105 distinguished from a polyamine by the functionality of the nitrogen atoms in the polymer. In a polyquaternary ammonium polymer most of the nitrogens are quaternized, i.e., they are covalently bonded to four carbon atoms. In a polyamite, most of the 110 nitrogen atoms are not quaternized. Polyamines will have nitrogen atoms which are primary, i.e., they are bonded to one carbon atom and two hydrogen atoms, secondary, i.e., they are bonded to two

carbons and one hydrogen, and tertiary, i.e., they are bonded to three carbons. In addition, polyamines may have some nitrogens which are quaternary; but these quaternary nitrogens will comprise considerably less than half of the total number of nitrogen atoms.

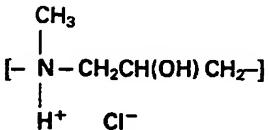
A polyquaternary ammonium polymer is made from a tertiary amine and another difunctional monomer, such as epichlorohydrin. The reaction 10 between the two monomers joins a carbon from the difunctional monomer to a nitrogen on a tertiary nitrogen to product a quaternary nitrogen.

In the process which produces polyamines only a minor amount of reactions occur which lead to 15 quaternary ammonium groups. In general, a polyamine is made from a multifunctional amine, such as diethylene triamine, which will contain some primary and some secondary nitrogens. The polymerization reactions between the multifunctional amines and difunctional monomers, such as 20 epichlorohydrins, will change primary nitrogens to secondary nitrogens and secondary nitrogens to tertiary nitrogens. Inevitably some of the tertiary nitrogens formed from previous reactions will be 25 converted to quaternary groups, but considerably less than half of the nitrogens will be quaternized.

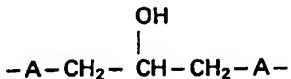
Polyamines may also be made from methylamine and epichlorohydrin, as taught by Nagy in U.S. Patent 3,567,659. In this process a deliberate attempt 30 is made to reduce the amount of cross-linkages by minimizing the formation of quaternary nitrogens. The polyamine made by Nagy has the structure



In solutions with an acid pH, these polyamines convert to the cationic form, e.g., the hydrochloride 35 salt.



The structure of a typical polyquaternary ammonium polymer used as a substrate in the present invention has the general formula



where A is a tertiary or quaternary nitrogen atom, 40 and in which the number of quaternary nitrogen atoms always exceeds the number of tertiary nitrogen atoms.

In processes employed to make polyquaternary ammonium polymers, a deliberate attempt is made 45 to have as many nitrogen atoms as possible in the quaternary form. Over fifty percent of the nitrogen atoms in polyquaternary ammonium polymers are quaternary nitrogen atoms.

The grafted portion of the polymers of the present

50 invention is made by the graft polymerization of water-soluble vinyl monomers on the backbone of the substrate. The water-soluble monomers employed in the present process include acrylamide, methacrylamide, acrylic acid, methacrylic acid, 55 dimethylaminoethyl methacrylate, N,N-dimethylacrylamide, dimethylaminopropylmethacrylamide, methacrylamidopropyltrimethylammonium chloride, dimethylallylammonium chloride, the quaternization product of dimethylaminoethyl methacrylate with methyl chloride, the quaternization product of dimethylaminoethyl methacrylate with dimethyl sulfate, and other water-soluble monomers which are readily apparent to those skilled in the art. Mixtures of two or more of the water-soluble vinyl 60 monomers may also be used.

Preferred mixtures include acrylamide with one or more of the other monomers listed above. Most preferred mixtures are acrylamide and acrylic acid, acrylamide and dimethylaminoethyl methacrylate, 65 acrylamide and the quaternization product of dimethylaminoethyl methacrylate with dimethyl sulfate, and acrylamide and the quaternization product of dimethylaminoethyl methacrylate with methyl chloride. Also included are mixtures of three or more 70 monomers, such as acrylamide, acrylic acid, and the quaternization product of dimethylaminoethyl methacrylate with dimethyl sulfate.

The graft polymerization can be initiated in one of several ways. High energy radiation such as gamma 75 rays or electrons accelerators are convenient methods to use in many graft polymerizations. Likewise, photochemical initiation is a convenient source of radicals which are effective in promoting graft polymerizations.

80 The preferred method to initiate polymerization to produce the cationic polyquaternary ammonium graft copolymers of the present invention is use of chemical catalysts. The reaction between ferrous ion and hydrogen peroxide is one such preferred 85 catalyst system. Other chemical catalysts are apparent to those skilled in the art.

A much preferred method to initiate these graft 90 polymerizations is by use of ceric salts. It is believed that ceric ion reacts with pendant hydroxyl groups 95 present in the substrate polymer. The hydroxyl groups result from the reaction of epichlorohydrin with a tertiary amine. The product of this reaction is a polymer containing alternating quaternary ammonium units with hydroxypropylene units.

100 The radical resulting from the reaction of ceric ion with the hydroxyl groups is reactive toward vinyl monomers. Polymerization then proceeds, adding further vinyl monomers and forming a new polymeric grafted chain one end of which is 105 covalently bonded to the substrate polymer. The result of this graft polymerization is the cationic polyquaternary ammonium graft copolymer of the present invention.

The reaction conditions can be varied over wide 110 limits. The graft copolymers of the present invention can be made under conditions in which the amounts, by weight, of the polyquaternary ammonium polymer (substrate) and the vinyl monomer (graft) are approximately equal. For example, the weight ratio

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of substrate to vinyl monomer may be in the range of, say, ten to one to one to ten. Graft copolymers with molecule weights up to one million or more are produced by this process.

5 We have found that even higher molecular weight grafts are produced when the weight ratio of substrate to monomer is substantially lower than one-to-ten. For example, exceptionally high molecular weight graft copolymers are produced when the 10 ratio of substrate to monomer is about one-to-fifty. Products made utilizing these ratios of reactants are quite effective flocculants.

If lower molecular weight products are desired, 15 high weight ratios of substrate to monomer are preferred. In addition, as taught by Nagy in U.S. Patent 3,711,573, isopropanol or other chain transfer agents may be added to the reaction mixture to reduce the molecular weight.

In general, it is desirable to have a final product 20 which has a high polymer solids content. Container costs and shipping costs of low solids content polymer solutions will increase the cost of the product and make it uneconomical even though the polymer properties may be superior. Water-soluble 25 polymers whose molecular weights are about one million or higher yield very viscous aqueous solutions. The upper limit of polymer content in an aqueous solution of a high molecular weight water-soluble polymer is less than ten percent for molecular 30 weights near one million. Solutions containing higher polymer solids content are too viscous for use in many situations.

In a preferred embodiment of the process for 35 making such high molecular weight graft copolymers while retaining high total polymer solids content, a small weight ratio of substrate polymer to monomer is employed. The total solids (substrate polymer plus monomer) is kept high, greater than ten percent. The reaction is initiated with ceric ion catalyst 40 and polymerization proceeds. To prevent gel formation, as the viscosity begins to build, additional low molecular weight polyquaternary ammonium polymer (substrate) is added. Since the polymer content of the substrate solution can be twenty-five 45 percent or higher, the total polymer solids content in the graft copolymer solution does not decrease. To further control the viscosity of the graft copolymer solution, isopropanol or other chain transfer agents may be added as well, either previous to, at the same 50 time as, or subsequent to the addition of the added polymer substrate solution.

Depending upon the amount of monomer in the 55 initial charge and the amount of polyquaternary ammonium substrate polymer added in the second charge, the final polymer solids content may vary from five to twenty-five percent or higher.

The conditions necessary for efficient graft 60 polymerization are not critical. The pH of the solution should be acidic, in the range of one to four pH units. The monomer need not be of high purity. For example, acrylamide is often supplied as a fifty percent aqueous solution containing copper ion as a polymerization inhibitor. While some advantage is gained by removal of the copper by ion-exchange in 65 that somewhat higher molecular weights are obtain-

able, this purification step is not critical or necessary.

Temperature is likewise not a critical parameter. Good grafting efficiency is obtained at ambient temperatures as well as at higher temperature.

70 Removal of oxygen from the solution is often employed so that higher molecular weight grafts are obtained, but this is not critical. Adequate polymerization efficiency and molecular weights are obtained when no effort is made to remove oxygen.

75 It is well recognized in the art that when two or more monomers are copolymerized, different properties are obtained when the relative concentrations of the monomers are different. The same holds true in graft copolymerizations. For certain applications,

80 e.g., sludge dewatering, it has been found that high ratios of a cationic monomer, such as the dimethyl sulfate quaternization product of dimethylaminoethyl methacrylate, to acrylamide will give a product having superior properties. For other applications, e.g. water clarification, best results have

85 been obtained when the grafted portion contains only small amounts of cationic monomer or even when the graft portion is completely non-ionic, i.e. a polyacrylamide graft.

90 In order to disclose the nature of the present invention still more clearly, the following illustrative examples will be given. It is to be understood, however, that the invention is not to be limited to the specific conditions or details set forth in these

95 examples except insofar as such limitations are specified in the appended claims.

Parts as used herein and in the appended claims are parts by weight.

EXAMPLE 1

100 This illustrates the preparation of a polyquaternary ammonium polymer which is suitable as the substrate polymer graft polymerizations.

An epichlorohydrin - methylamine prepolymer was prepared by reacting 800 parts of a fifty percent 105 aqueous methylamine solution with 2424 parts of epichlorohydrin. The reaction was carried out at 35°C in 600 parts of n- propanol solvent. When the reaction was completed, 272 parts of concentrated sulfuric acid was added.

110 The polyquaternary ammonium polymer was then prepared by adding 2007 parts of water and 2275 parts of an aqueous solution containing 60 percent N,N,N',N' - tetramethylethylenediamine. The mixture was heated to 70-75°C until the contents of the

115 vessel became viscous, at which point the reactants were diluted with 7678 parts of water. The mixture was reheated and the reaction continued until the viscosity increased again. The polymerization reaction was stopped by adding 402 parts of sulfuric acid

120 and 298 parts of water. The final solution contained 25 percent by weight of polymeric solids. Over eighty percent of the nitrogen atoms in this polymer are quaternary nitrogen atoms.

EXAMPLE 2

125 This example describes a method for the preparation of a graft copolymer of the present invention.

Into a one liter glass reaction kettle fitted with an agitator, thermometer, and nitrogen sparge tube was added 250 grams of the polyquaternary ammonium polymer of Example 1, 100 grams of a 50

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percent aqueous acrylamide solution, and 147 grams of deionized water. The solution was agitated and purged with nitrogen to remove dissolved air. Into this mixture was added three milliliters of a 5 catalyst solution consisting of 0.1 N ceric ammonium nitrate in 1 N nitric acid.

A reaction occurred immediately. The temperature rose and the solution became very viscous in about five minutes. The reaction was allowed to continue 10 for two hours. The resulting solution contained 22.5 percent of the polyquaternary ammonium-acrylamide graft copolymer wherein about 55.6 percent of the graft copolymer arises from the substrate and about 44.4 percent of the graft copolymer is polymerized acrylamide.

EXAMPLE 3

This example describes the preparation of another polyquaternary ammonium polymer which is suitable as a substrate in subsequent graft polymeriza- 20 tions.

The ionene polymer, poly[hydroxyethylene-(dimethylimino)ethylene(dimethylimino)methylene dichloride] was prepared by mixing 375 parts of an aqueous solution containing 60 percent of N,N,N',N'- 25 -tetramethylethylenediamine (TMEDA) and 4496 parts of muriatic acid (31.5 percent HCl) at a temperature below 50°C. While the temperature was maintained at 40°-50°C by cooling, 3588 parts of epichlorohydrin were added. The mixture was further agitated for one-half hour and then heated to 30 60°-70°C at which temperature it was maintained while 3750 parts of additional aqueous solution of TMEDA were added. The concentration was adjusted to 60 percent polymer solids by distilling 35 some of the water from the product. The molecular weight of the product is about 5,000. All of the nitrogen atoms in this polymer are quaternary nitrogen atoms.

EXAMPLE 4

40 This illustrates a method for the preparation of

graft copolymers using as the substrate the polymer of Example 3.

The general procedure of Example 2 was used except that 313 grams of water, 100 grams of a 50 percent acrylamide solution, and 84 grams of the polyquaternary ammonium polymer of Example 3 were added to the reaction kettle. Three milliliters of ceric catalyst were added and a viscous polymer solution was produced in a few minutes. Twenty-five 50 minutes after the addition of the first three milliliters of catalyst, another three milliliters of catalyst were added. Twenty-five minutes after this second catalyst charge, another three milliliters of ceric catalyst were added. The resulting clear, viscous 55 solution was approximately 20.1 percent polymer by weight wherein approximately half was grafted acrylamide and the remainder came from the substrate polyquaternary ammonium polymer of Example 3.

60 **EXAMPLES 5-11**
The general procedure of Example 2 was utilized except that 118.5 grams of water, 7.5 grams of isopropanol, 70 grams of acrylamide, and 250 grams of the polyquaternary polymer of Example 1 were agitated in the reaction flask. In addition to the acrylamide, the water-soluble vinyl addition monomers listed in Table 1 were utilized in separate preparations. In each case, 30 grams of the listed monomers were added. Three milliliters of ceric catalyst were added. In each case the temperature rose, and the solution became viscous, indicating that a graft polymerization occurred. Additional ceric catalyst (three milliliters per each addition) was added. A total of 24 milliliters of catalyst was added to each except for Example 11 where only 12 milliliters were added. In this case, the solution was already extremely viscous.

Table 1

Example	Comonomer Used with Acrylamide To Form Graft Copolymer	Total Polymer Solids
5	dimethylaminoethylmethacrylate methosulfate (80% solution)	24.3
6	dimethylaminoethylmethacrylate methylchloride (75% solution)	24.0
7	dimethylaminopropylmethacrylamide	25.5
8	methacrylamidopropyltrimethyl ammonium chloride (50% solution)	22.5
9	dimethylallylammonium chloride	25.5
10	N,N dimethylacrylamide	25.5
11	acrylic acid	26.1

EXAMPLE 12

The procedure of Example 2 was followed with the 80 exception that the ceric catalyst was not used. Into the reaction kettle were added 250 g of the polyquaternary ammonium polymer of Example 1, 100 g of a 50 percent acrylamide solution and 147 g of water. The pH was adjusted to 3.5 with 50 percent sodium 85 hydroxide.

Two milliliters of 0.35 percent hydrogen peroxide were added to the flask, quickly followed by two milliliters of a solution consisting of 0.1 M ferrous ammonium sulfate in 1 M sulfuric acid. An immediate temperature rise occurred, accompanied by an increase in viscosity. The reaction was allowed to continue for forty minutes after which 7.5 milliliters of isopropanol were added, followed by an additional

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charge of the catalyst, that is, two milliliters of 0.35 percent hydrogen peroxide and two milliliters of the ferrous solution. During the next two hours two more additions of the catalyst system (ferrous solution and H₂O₂) were made. The resulting solution was similar in appearance and composition to the product of Example 2, except that the product of this example contains slightly less polymer solids, 21.6 percent.

10 **EXAMPLE 13**

The following example describes the preparation of the polyquaternary ammonium graft copolymer of the present invention utilizing a combination of two catalyst systems.

15 The same procedure of Example 2 was followed. Into the reaction kettle was added 250 g of the polymer of Example 1, 100 g of a 50 percent acrylamide solution and 147 g of water. Three milliliters of the ceric catalyst were added. The 20 temperature rose and the solution became viscous. Two hours after the reaction was initiated, 7.5 milliliters of isopropanol were added, followed by two milliliters of 0.35 percent hydrogen peroxide and two milliliters of the ferrous sulfate described in 25 Example 12. A substantial amount of unreacted monomer was present following the first addition of the ceric catalyst since an immediate rise in temperature and a slight increase in viscosity occurred. Two more additions of two milliliters of each of the 30 peroxide and ferrous solutions were made. No obvious reaction occurred following the last catalyst addition. The product of this Example was very similar in appearance and composition to the product of Example 12.

35 **EXAMPLE 14**

The following illustrates another method for preparation of the graft copolymers of the present invention.

40 The general procedure of Example 2 was followed except that two reaction kettles were charged with 100 g of a 50 percent acrylamide solution, 147 g of water and 4 g of the polyquaternary ammonium polymer of Example 1. The ratio of acrylamide to polyquaternary ammonium polymer was, therefore, 45 50 to 1 on a solids basis. Three milliliters of ceric catalyst solution were added to each kettle. An immediate increase in temperature occurred in each solution, followed by a rapid increase in viscosity. When the viscosity became so great that the solution 50 to climb the agitator shaft, 250 milliliters of water were added to the first kettle, Solution 14A, and 250

milliliters of the polyquaternary ammonium polymer of Example 1 were added to the second kettle, Solution 14B. The reactions continued as evidenced 55 by a slow climb in temperature and a noticeable increase in viscosity. Two hours after the initial charges of catalyst, an additional 300 milliliters of water were added to Solution 14A. Then to each solution 7.5 milliliters of isopropanol were added, 60 followed by the addition of two milliliters of dilute hydrogen peroxide and two milliliters of the ferrous solution described in Example 12. A second charge of two milliliters of each of the ferrous solution and the peroxide solution was made to each solution. 65 The resulting solutions were approximately 6.3 percent polymer solids for Solution 14A and 21.8 percent in Solution 14B.

EXAMPLE 15

The polyquaternary ammonium graft polymers of 70 this invention were tested for their effectiveness as flocculants in laboratory jar tests. Fifteen hundred milliliters of a 0.4 percent by weight suspension of Fuller's Earth (Kaolin) were added to each jar and agitated by paddles turning at 100 rpm. Varying 75 quantities of the polymer solution to be tested were added and agitation was continued for one minute after which agitation was stopped and the suspension allowed to settle for five minutes. Observations were made on the flocculation speed, i.e. the settling 80 rate, as well as the final clarity of the supernatant solution after five minutes.

The flocculation speed was judged qualitatively and the polymers were ranked in order of their flocculation speed. The clarity of the test solution 85 was graded on a scale of 0 to 5 (0 means no settling and 5 signifies a clear supernatant layer) after allowing for settling for five minutes.

Table 2 compares the qualities of the graft copolymer prepared in Example 2 with two commercially 90 available products both of which are used to treat water, to remove suspended matter. Commercial product A is 25 percent by weight and commercial product B is 40 percent by weight of polymer solids. A dilute solution (1500 ppm) of each polymeric 95 product to be tested was first made up. Then 2, 4, or 8 milliliters of these dilute polymer solutions were added to the Kaolin suspension. The usage rate of each polymeric dilution product was, therefore, 2, 4, or 8 ppm. However, since the products differ on a 100 percent solids basis, usage rate on a total polymer solids basis is, of course, different.

Table 2

	Clarity Rating at Usage Rate of		
	2 ppm	4 ppm	8 ppm
Product of Example 2 (22.5 percent)	3.1	3.5	4.4
Commercial Product A (25 percent)	3.4	3.8	3.5
Commercial Product B (40 percent)	3.2	3.4	3.3

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The product of Example 2 at each usage rate gave the fastest settling rate. It is seen in Table 2 that the two commercial products give good clarity at these usage rates with a maximum effect near 4 ppm. The 5 product of Example 2, in addition to having the fastest settling rates, gives substantially better clarity at somewhat higher usage rates, with no decrease in effectiveness at higher usage rates. Excellent effectiveness occurs over a wider range in 10 usage rates.

EXAMPLE 16
This illustrates the effectiveness of the polyquaternary ammonium graft copolymers in flocculating suspended matter when the grafted portion of the 15 polymeric product is a mixture of acrylamide and other water-soluble vinyl addition monomers.
The procedure of Example 15 was followed. Polymer solutions tested were made from the products of Example 5 through 10, as well as Example 2. 20 The results are shown in Table 3 below.

Table 3

Example	Comonomer	Clarity at Usage Rate of	
		2 ppm	5 ppm
2	Acrylamide alone	3.1	4.0
5	Dimethylaminoethyl methacrylate methosulfate	3.4	4.2
6	Dimethylaminoethyl methacrylate methylchloride	3.1	4.0
7	Dimethylaminopropyl methacrylamide	2.8	3.7
8	Methacrylamidiopropyl trimethyl ammonium chloride	2.9	3.8
9	Dimethyldiallyl ammonium chloride	2.8	3.8
10	N,N Dimethylacrylamide	2.9	3.9

All of the graft copolymers in the table above show excellent flocculating properties.

EXAMPLE 17

This example illustrates the effectiveness of the 25 graft copolymers of the present invention as flocculants for sewage sludge.

The apparatus consisted of No. 1 Büchner funnel positioned directly over a 250 ml graduated cylinder. A piece of filter cloth was cut to the same dimension 30 as No. 1 filter paper and this filter cloth was placed in the Büchner funnel. This filter cloth was of the same type used in sludge dewatering presses.

Five percent dilutions of the polymer solutions to be tested were prepared. For each test 500 milliliters 35 of sewage sludge (3.4 percent solids) were placed in a beaker. The desired amount of dilute polymer solution was placed in a second beaker. The sludge was then poured back and forth between the beakers three times to ensure complete mixing. The resulting 40 mixture was then poured onto the filter cloth in the Büchner funnel.

The solution was allowed to drain by gravity, i.e., no pressure or vacuum was applied. The amount of liquid collected in the graduated cylinder was recorded after 15, 30, 60 and 120 seconds. The better the sludge dewatering effectiveness of the polymer, the more liquid will be collected at any given time.

Two graft polymers were prepared for testing. The procedure of Example 6 was used to make Solution 50 D. The reaction kettle was charged with 147 g of water, 250 g of the polyquaternary ammonium polymer of Example 1, 70 g of a 50 percent acrylamide solution, and 30 g of an 80 percent aqueous solution of dimethylaminoethyl-methylacrylate methosulfate. Ceric catalyst was 55

added nine times in three milliliter increments over the next four hours.

Solution E was prepared in a slightly larger scale. A two-liter reaction kettle was charged with 828 g of 60 water, 1000 g of the polyquaternary ammonium polymer of Example 1, 160 g of a 50 percent acrylamide solution and 40 g of isopropanol. Twelve milliliters of ceric catalyst were added.

Table 4 shows the sludge dewatering effectiveness of Solutions D and E compared to the effectiveness of a commercially available cationic polyacrylamide polymer used in sludge dewatering operations.

Table 4

Solution Tested	Volume of 5% Polymer Solution Added	Volume in Milliliters Collected After			
		Milliliters	15 sec.	30 sec.	60 sec.
Solution D	4	26	38	53	73
	6	45	65	78	93
	8	60	80	98	116
Solution E	4	27	35	50	65
	6	50	65	83	100
	8	55	75	93	105
Commercial	4	19	23	31	41
Cationic	6	32	45	60	75
Polyacrylamide	8	52	70	85	101

The table demonstrates that graft copolymers of the present invention are effective in dewatering sewage sludge.

EXAMPLE 18

5 The polymeric mixtures of Example 15 of this invention were tested for their effectiveness in the retention of total solids in a paper pulp slurry using the method described in Example 15 of U.S. Patent 4,250,269 which disclosure is hereby made a part of 10 this application.

Fractionation of the paper pulp slurry showed that the slurry contained 27 percent fines. Percent fines retention could then be calculated once the total solids retention and the percent fines in the original 15 slurry were known. Table 5 shows that the polyquaternary ammonium acrylamide graft copolymer of Example 2 is superior to the ungrafted polyquaternary ammonium polymer of Example 1, a product which is presently used as a retention aid.

Table 5

Product Tested	Use Rate Pounds per Ton of Pulp	Percent Retention of Fines
Control with no retention aid	0	59.6
Example 1	0.75	65.3
	1.50	69.6
	2.50	71.5
	5.00	71.2
Example 2	0.675	67.3
	1.35	69.2
	2.25	74.3
	4.50	81.8

EXAMPLE 19

20 This example illustrates the effectiveness of the graft copolymers of the present invention in increasing the dry strength of paper.

Handsheets were made and tested using a Scott Internal Bond Tester. Three hundred grams of a 1.5 percent hardwood Kraft pulp which was refined to a Canadian Stand Freeness of 540 milliliters were added to 300 milliliters of water. The desired amount of diluted polymer solution was added to achieve the 30 usage rates shown in Table 6 below. Solutions

tested were the product of Example 2 wherein the grafted portion comprises acrylamide alone, the product of Example 7 wherein the grafted portion comprises acrylamide and dimethylaminomethacrylate methyl chloride, and the product of Example 11 wherein the grafted portion comprises acrylamide and N,N-dimethylacrylamide. The graft copolymers listed above were compared to the product of Example 1, an ungrafted polyquaternary ammonium 40 polymer which is presently used by the paper industry to increase bond strength.

Table 6

Product Tested	Use Rate Pounds per Ton of Pulp	Increase in Percent Scott Bond Strength
Example 1	10	14
Example 2	10	16
Example 7	10	24
Example 11	10	18

The graft copolymers of the present invention give increased bond strength and the presence of cationic comonomers in the grafted portion brings about the 45 best improvement.

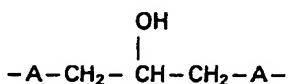
While particular embodiments of the invention have been described, it will be understood, of course, that the invention is not limited thereto since many modifications may be made thereof. It is, 50 therefore, contemplated to cover by the appended claims any such modifications as fall within the true spirit and scope of the invention.

The invention having thus been described, what is claimed and desired to be secured by Letters Patent 55 is:

CLAIMS

1. A water-soluble high-molecular-weight quaternary ammonium graft copolymer comprising a substrate portion and a graft portion, the substrate portion being derived from a water-soluble 60 polymeric quaternary ammonium composition having a plurality of hydroxypropylene groups with the structure

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wherein A is a tertiary or quaternary nitrogen atom, and in which the number of quaternary nitrogen atoms exceeds the number of tertiary nitrogen atoms, and the graft portion being derived from a 5 polymeric composition comprising polymerised water-soluble nonionic, anionic and/or cationic vinyl addition monomers, the ratio of graft portion to substrate portion varying from 1:10 to 100:1 by weight.

10 2. A graft copolymer as claimed in claim 1 wherein the graft portion is derived from polyacrylamide.

3. A graft copolymer as claimed in claim 1 wherein the graft portion is derived from a copolymer 15 of acrylamide and acrylic acid.

4. A graft copolymer as claimed in claim 1 wherein the graft portion is derived from a copolymer of acrylamide and the quaternization product of dimethylaminoethyl methacrylate with dimethyl sulfide.

20 5. A graft copolymer as claimed in claim 1 wherein the graft portion is derived from a copolymer of acrylamide and the quaternization product of dimethylaminoethyl methacrylate with methyl chloride.

6. A graft copolymer as claimed in claim 1 wherein the graft portion is derived from a terpolymer of acrylamide, acrylic acid, and the quaternization product of dimethylaminoethyl methacrylate with 25 dimethyl sulfate.

7. A graft copolymer as claimed in claim 1 wherein the graft portion is derived from a terpolymer of acrylamide, acrylic acid, and the quaternization product of dimethylaminoethyl methacrylate with 30 methyl chloride.

8. A graft copolymer as claimed in any one of the preceding claims wherein the substrate portion comprises a water-soluble polymeric quaternary ammonium composition derived from methylamine, 40 epichlorohydrin and N,N,N',N'- tetramethyl-ethylenediamine.

9. A graft copolymer as claimed in any one of claims 1 to 7 wherein the substrate portion comprises a water-soluble polymeric quaternary ammonium 45 composition derived from epichlorohydrin and N,N,N',N'- tetramethyl-ethylenediamine.

10. A graft copolymer as claimed in claim 1 wherein the substrate portion comprises a water-soluble polymeric quaternary ammonium composition 50 derived from methylene, epichlorohydrin and N,N,N',N'- tetramethyl-ethylenediamine and the graft portion is derived from polyacrylamide.

11. A graft polymer as claimed in claim 1 substantially as herein described with reference to 55 Examples 2 and 4-15.

12. A process for the preparation of a graft copolymer as claimed in any one of claims 1-11 which comprises reacting a water-soluble polymeric quaternary ammonium composition as defined in 60 claim 1 with one or more water-soluble nonionic, anionic or cationic vinyl addition monomers, in the

presence of a polymerisation catalyst.

13. A process as claimed in claim 12 wherein the catalyst comprises a system generating ceric ion.

65 14. A process as claimed in claim 12 wherein the catalyst comprises a ferrous salt and hydrogen peroxide.

15. A process as claimed in claim 12 substantially as herein described.

70 16. A process as claimed in claim 12 substantially as herein described in any one of Examples 2 and 4-15.

17. A graft copolymer defined in claim 1 whenever prepared by a process as claimed in any one of 75 claims 12-16.

18. A method of increasing the rate of water removal from wet fibrous webs during the manufacture of paper and paperboard which comprises adding to the papermaking system a graft copolymer as claimed in any one of claims 1 to 11 in an amount sufficient to achieve the desired increase of water removal.

19. A method of improving the retention of the components of a papermaking furnish in the wet 80 fibrous web during the manufacture of paper and paperboard which comprises adding to the papermaking system a graft copolymer as claimed in any one of claims 1 to 11 in an amount sufficient to achieve the desired increase in retention.

20. A method of increasing the strength of paper and paperboard which comprises adding to the papermaking system a graft copolymer as claimed in any one of claims 1 to 11 in an amount sufficient to achieve the desired increase in strength.

90 21. A method of sizing paper or paperboard which comprises adding to the papermaking system a graft copolymer as claimed in any one of claims 1 to 11 in an amount sufficient to size said paper and paperboard.

100 22. A method of flocculating solids from an aqueous system containing suspended or dissolved solids which comprises adding to said aqueous system as a flocculant a graft polymer as claimed in any one of claims 1 to 11 in an amount sufficient to cause flocculation of said solids.

23. A method of increasing the rate of water removal during the dewatering of wet sludges which comprises adding to the wet sludges a graft copolymer as claimed in any one of claims 1 to 11 in an 105 amount sufficient to increase the rate of water removal.

24. A method as claimed in claim 23 wherein the wet sludges are derived from municipal and/or industrial effluent.

110 25. Paper or paperboard whenever manufactured by a process employing, as an additive, a graft copolymer as claimed in any one of claims 1 to 11.

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